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The University of Chicago.
Founded by JOHN D. ROCKEFELLER.

On Sodium Phenyl and the Action of Sodium on Ketones.

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

DEPARTMENT OF CHEMISTRY.

BY S. F. ACREE.

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On Sodium Phenyl and the Action of Sodium on Ketones.

The following work was undertaken at the suggestion and under the direction of Dr. J. U. Nef. Its object was to prepare sodium phenyl and to ascertain whether it is formed as an intermediate product in various reactions in which brombenzene and sodium are used. Nef came to the conclusion, from his experiments with sodium phenylacetylene, that sodium phenyl must first be formed in every case,[1]

$$C_6H_5Br + Na_2 = C_6H_5—Na + NaBr,$$

and that this substance subsequently reacts with other reagents that may be present, as alkyl haloids (Fittig), ketones (Frey),[2] carbon dioxide (Kekulé), chlorcarbonic ether (Wurtz).

We have since succeeded in preparing sodium phenyl from mercury phenyl and sodium. It reacts with alkyl, aryl, and acyl halides, with ketones and other reagents, giving practically the same products which are formed when these reagents are treated in ethereal solution with brombenzene and sodium; hence it may be concluded that in those reactions where brombenzene and sodium are used (Fittig's, Frey's, Kekulé's, Wurtz's reactions), sodium phenyl is the intermediate product.

Nef has shown[3] that the reactions of the primary and secondary alkyl haloids with other substances such as alcoholates, amines, etc., depend upon the dissociation of the alkyl haloid into alkylidene and halogen hydride. The halogen hydride is neutralized by the alcoholate, amine, etc., while the alkylidene absorbs the alcohol, amine, etc., that is present, by addition (alkylation). In some cases the alkylidene may also, in part, rearrange to an olefine or polymerize to a dialkylidene.

[1] Nef: Ann. Chem. (Liebig), **308**, 281, 291.
[2] Frey: Ber. d. chem. Ges., **28**, 2514.
[3] Ann. Chem. (Liebig), **309**, 126, **318**, 2.

Sodium phenyl should, from this point of view, interact with primary and secondary alkyl haloids, *e. g.*, ethyl iodide, as follows:

I. $2C_6H_5—Na + 2C_2H_5I = 2C_6H_5—Na + 2CH_3CH\rightleftarrows + 2HI$;

II. $CH_3CH\rightleftarrows + Na—C_6H_5$ or $H—C_6H_5 =$
$CH_3CH—C_6H_5$ or $CH_3CH_2C_6H_5$;
$\dot{N}a$

III. $Na—C_6H_5 + HI$ or $CH_3CHNaC_6H_5 + HI =$
C_6H_6 or $C_6H_5CH_2CH_3 + NaI$.

Part of the ethylidene may also go over into ethylene by intramolecular alkylation, or in the case of benzyl chloride the phenylmethylene may polymerize in part to stilbene.[1]

These expectations were in every way realized. It is surprising with what intense violence the interactions of sodium phenyl take place even with an inactive substance like brombenzene.

Preparation of Sodium Phenyl.

When mercury diphenyl is dissolved in dry benzene or ligroin and treated in a flask with a return-condenser, with considerably more than the molecular quantity of fine sodium wire, the sodium reacts vigorously with the mercury diphenyl. Sodium amalgam is formed and falls to the bottom of the flask, while a light-brown powder, sodium phenyl, remains suspended in the solution. The larger the amount of sodium used, the more nearly complete is the reaction,

$$Hg(C_6H_5)_2 + 2Na_2 = HgNa_2 + 2NaC_6H_5.$$

That this powder is sodium phenyl and not sodium mercury phenyl, corresponding to sodium zinc ethyl,[2] was proved by analysis. One sample was made up especially for analysis, as follows: Five grams of mercury diphenyl, dissolved in 100 cc. of benzene, were boiled with five grams of sodium wire until the reaction was complete. Upon adding 2 grams of sodium wire and boiling again there was hardly any action. This showed that very little mercury diphenyl had failed to

[1] Nef: *Loc. cit.*

[2] Wanklyn: Ann. Chem. (Liebig), 108, 67; Z, 1866, p. 253.

react with the first portion of sodium. As sodium phenyl is very readily decomposed by the moisture of the air, the analysis was accomplished as follows: A 50 cc. dropping-bottle was fitted with a stop-cock and a stream of dry hydrogen was passed through the bottle; it was then weighed. Part of the sodium phenyl, together with some benzene, was withdrawn from the flask by means of a pipette and transferred to the dropping-bottle. The benzene was then distilled from the dropping-bottle in a stream of hydrogen, leaving behind the sodium phenyl as a dry powder. The dropping-bottle was again weighed, the difference between the two weights giving the amount of the sodium phenyl. When water was added to the dropping-bottle the sodium phenyl was decomposed, forming sodium hydroxide and benzene. The sodium hydroxide was titrated with N/1 sulphuric acid and phenolphthalein. There was a small amount of mercury diphenyl, insoluble in water, left in the dropping-bottle. This showed that the sodium phenyl was not quite pure, and accounts for the low results obtained in the analyses.

Analysis of first preparation:

I. 0.5793 gram substance required 5.70 cc. N/1 sulphuric acid.

II. 0.4329 gram substance required 4.20 cc. N/1 sulphuric acid.

	Calculated for NaC_6H_5.	Found. I.	II.
Na	23.04	22.68	22.36

Analysis of other preparations:

I. 0.3525 gram substance required 3.07 cc. N/1 sulphuric acid.

II. 0.6843 gram substance required 6.47 cc. N/1 sulphuric acid.

	Calculated for NaC_6H_5.	Found. I.	II.
Na	23.04	20.07	21.79

As sodium mercury phenyl, $NaC_6H_5—Hg(C_6H_5)_2$, has only 5.07 per cent of sodium, the above analyses show beyond doubt that the powder is sodium phenyl containing traces of

mercury diphenyl. When sodium phenyl is exposed to the air on a filter-paper for a short time, it catches fire. As it is decomposed by water, the reactions were always carried out in the flask in which the sodium phenyl had been prepared, a calcium chloride tube being connected with the flask to prevent access of moisture.

Action of Sodium Phenyl on Ethyl Bromide and on Ethyl Iodide.

By carefully fractionating some low-boiling ligroin a product was obtained that boiled between 54° and 63°. 4.5 grams of mercury diphenyl were dissolved in about 50 cc. of this ligroin and converted into sodium phenyl in the usual way. The flask was then fitted with a dropping-funnel and connected with bromine absorption-tubes to absorb any ethylene formed. 2.5 grams of ethyl bromide were then added slowly through the dropping-funnel, the flask being kept cold by a freezing-mixture. The solution was then warmed to 40° to drive off any ethylene. On treating the bromine in the absorption-tubes with sodium hydroxide a few drops of ethylene dibromide, boiling at about 130°, were obtained. The ligroin solution was very carefully fractionated. After the main portion had distilled over there was a fraction at 80° to 90°, indicating that benzene was present, but this was not proved. The remainder, by repeated fractionation, gave 2 grams of ethylbenzene, boiling at 130° to 135°. It was treated with nitric acid (20 per cent) in a sealed tube, at 160°, for six hours, and when the tube was opened a great deal of gas escaped. Not all of the ethylbenzene had been decomposed, but 0.5 gram of benzoic acid, melting at 119°, was obtained.

Sodium phenyl and ethyl bromide give, therefore, ethylbenzene and small amounts of benzene and ethylene.

Sodium phenyl (5 grams suspended in ligroin (boiling-point 35° to 40°) was treated with the molecular quantity of ethyl iodide in absolute ether, the flask being kept cold. The flask was then connected with bromine absorption-tubes and warmed. Upon treating the bromine with sodium hydroxide only a drop or two of ethylene dibromide remained. When the ligroin solution was fractionated, 2 grams of ethylbenzene,

boiling at 130° to 135°, were obtained. Heated with nitric acid, of sp. gr. 1.30, in a sealed tube for six hours at 160°, it gave 1.1 grams of pure benzoic acid melting at 122°.

Action of Sodium Phenyl on Isoamyl Iodide.

Sodium phenyl (5 grams) prepared in ligroin (boiling-point 55° to 60°) was treated with the molecular quantity of isoamyl iodide in absolute ether, the flask being well cooled by a freezing-mixture. When the reaction was over, the flask was connected with a bromine absorption-apparatus and warmed for some time. The bromine was treated with sodium hydroxide, and 1.1 grams of isoamylene dibromide, of boiling-point 62° to 64° at 15 mm., were obtained. When the ligroin filtrate was distilled a fraction boiling between 80° and 90° was obtained, indicating the formation of benzene in the reaction. Three grams of oil boiling between 175° and 200° were also obtained. This, by refractionation, gave 2 grams of isoamylbenzene, boiling at 190° to 195° (mostly at 193°).

Sodium phenyl and isoamyl iodide, therefore, give benzene, isoamylene, and isoamylbenzene.

Analysis of isoamylene dibromide:

0.8014 gram substance gave 1.3095 gram AgBr by Carius' method.

	Calculated for $C_5H_{10}Br_2$.	Found.
Br	69.56	69.53

Analysis of isoamylbenzene:

0.2710 gram substance gave 0.8817 gram CO_2 and 0.2658 gram H_2O.

	Calculated for $C_{11}H_{16}$.	Found.
C	89.09	88.73
H	10.91	10.90

Action of Sodium Phenyl on Benzyl Chloride.

When 5 grams of sodium phenyl, prepared in ligroin (boiling-point 55° to 60°), were treated with the molecular quantity of benzyl chloride there was a vigorous reaction. The ligroin filtrate gave, on distillation, 1 gram of a substance having the

boiling-point 250° to 270° (diphenylmethane). At 300° to 320° a fraction passed over, which partly solidified. When dried, this melted between 115° and 125° and was shown to be stilbene by its conversion into stilbene dibromide (0.5 gram, melting-point 237°, being obtained). On refractionation, 0.8 gram of diphenylmethane, boiling at 260° to 265°, was obtained, which had the characteristic odor of this substance and which solidified when cooled.

Sodium phenyl and benzyl chloride, therefore, give diphenylmethane and stilbene.

Analysis of diphenylmethane:

0.2230 gram substance gave 0.7584 gram CO_2 and 0.1496 gram H_2O.

	Calculated for $C_{13}H_{12}$.	Found.
C	92.80	92.76
H	7.20	7.45

Action of Sodium Phenyl on Brombenzene.

Sodium phenyl (5 grams) prepared in ligroin (boiling-point 60° to 80°) was treated with 7 grams (1 molecule) of brombenzene in ether. As the reaction was very vigorous, the flask was kept cool by a freezing-mixture. The solution, when distilled, gave 1.1 grams of diphenyl, boiling at 250° to 260°. This solidified and melted at 69° to 70°. Mixed with a sample of Kahlbaum's diphenyl the melting-point was not lowered. There was a considerable fraction above 300°, but it was a resinous liquid that would not solidify.

Analysis:

0.2397 gram substance gave 0.8203 gram CO_2 and 0.1410 gram H_2O.

	Calculated for $C_{12}H_{10}$.	Found.
C	93.45	93.33
H	6.55	6.54

Action of Sodium Phenyl on Benzophenone.

Frey[1] found that when benzophenone is treated with molecular quantities of brombenzene and sodium in absolute ether, a quantitative yield of triphenylcarbinol is obtained. This

[1] Frey: Ber. d. chem. Ges., 28, 2514.

has been confirmed. Similar carbinols are obtained when homologues of benzophenone and brombenzene are treated with sodium in the same way. Nef[1] explained this reaction on the basis of an intermediate formation of sodium phenyl, which is subsequently absorbed by the ketone, forming the sodium salt of the carbinol.

$$R—Na + R_2C=O \rightarrow R_3\equiv CONa.$$

This is proved by what follows :

Mercury diphenyl (5 grams) was treated with sodium wire (5 grams) in benzene, and then 2 grams of solid benzophenone were slowly added with constant shaking and cooling. The mixture was treated with water and sodium carbonate, and the benzene solution then dehydrated and distilled. A residue was obtained which, when recrystallized from ligroin, gave 2.5 grams of triphenylcarbinol, melting at 162°. The ligroin filtrate was evaporated and the residue was digested with phenylhydrazine and absolute alcohol, 0.25 gram of benzophenonephenylhydrazone (melting-point 130°) being obtained. This shows that not all of the benzophenone had been acted upon by the sodium phenyl. A small amount of benzoic acid was obtained by acidifying the sodium carbonate solution. Two grams of benzophenone should give 2.86 grams of triphenylcarbinol. When we take into consideration the small amount of recovered benzophenone and the benzoic acid, the yield of triphenylcarbinol actually obtained, 2.5 grams, is nearly quantitative.

Analysis :

0.2382 gram substance gave 0.7644 gram CO_2 and 0.1357 gram H_2O.

	Calculated for $C_{19}H_{16}O$.	Found.
C	87.62	87.52
H	6.21	6.33

The Action of Brombenzene and Sodium on Benzpinacone.

Benzpinacone (5 grams) in absolute ether was allowed to stand fourteen hours, in a sealed vessel, with 2.5 grams of

[1] Nef : Ann. Chem. (Liebig), 308, 291.

brombenzene (1 molecule) and 1 gram of fine sodium wire (1 molecule). The reaction-product was poured into water and treated with sodium carbonate, but no benzoic acid was found in the alkaline solution. When the ether was evaporated and the residue recrystallized from alcohol, 2.4 grams of triphenylcarbinol, melting at 158°, were obtained. On adding water to the alcoholic filtrate a precipitate of benzhydrol was obtained, which, when recrystallized from ligroin, weighed 2.2 grams. It melted at 67° and gave a blood-red color with concentrated sulphuric acid. Benzpinacone is known to dissociate completely into benzophenone and benzhydrol at its melting-point, 185°, or on heating with alcoholic potash.[1] The above experiment shows that this dissociation takes place at room temperature. As fast as benzophenone is formed it reacts with the sodium phenyl (from brombenzene and sodium), giving triphenylcarbinol.

Analysis of benzhydrol :

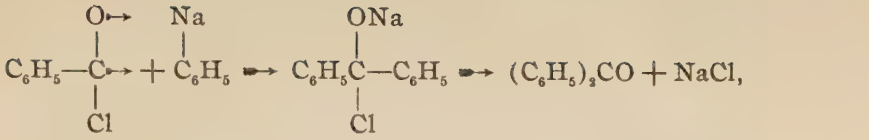
0.2542 gram substance gave 0.7908 gram CO_2 and 0.1494 gram H_2O.

	Calculated for $C_{13}H_{12}O$.	Found.
C	84.73	84.84
H	6.58	6.53

Action of Sodium Phenyl on Benzoyl Chloride.

Mercury diphenyl (4.5 grams) was converted into sodium phenyl in benzene and treated with 1.5 grams of redistilled benzoyl chloride dissolved in absolute ether. The reaction was very vigorous. The mixture was poured into water and extracted with sodium carbonate, but very little benzoic acid was obtained. The benzene was distilled off. The residue, when recrystallized from alcohol, gave 1.5 grams of triphenylcarbinol melting at 156°. The alcoholic filtrate was boiled with phenylhydrazine, but no benzophenonephenylhydrazone was obtained. This shows that the benzophenone first formed from the benzoyl chloride and sodium phenyl, according to the equation,

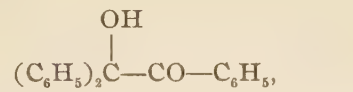
[1] Thörner and Zincke : Ber. d. chem. Ges., 10, 1474.



reacts immediately with more sodium phenyl, giving triphenylcarbinol.

Action of Sodium Phenyl, and of Brombenzene and Sodium, on Benzil.

Eight grams of mercury diphenyl were converted into sodium phenyl in ligroin (boiling-point 60° to 80°) solution. Solid benzil (5 grams, melting-point 96°) was slowly added with constant stirring and cooling. The reaction took place instantly, a beautiful violet-colored solid being formed. The mass was poured into water, extracted with sodium carbonate, and the ligroin solution was dried with calcium chloride and distilled on a water-bath. When acidified, the sodium carbonate extract gave 1.5 grams of benzoic acid, which melted at 121° when recrystallized. The residue from the ligroin was treated with cold absolute alcohol; no residue of benzpinacone was left. The residue obtained by evaporating the alcohol consisted of a mixture of phenylbenzoin,[1]



and triphenylcarbinol. These are readily separated by fractional crystallization from ligroin (boiling-point 60° to 80°) or alcohol, in which solvents the phenylbenzoin is by far the more soluble. Thus 1.5 grams of phenylbenzoin, melting-point 84°, and 1.3 grams of triphenylcarbinol, melting-point 155°, were obtained, besides a considerable amount of a resinous product that could not be made to crystallize.

The same products were obtained when benzil was treated with brombenzene and sodium in absolute ether. To 5 grams of benzil in absolute ether were added 4 grams (1 molecule) of brombenzene and 1 gram (1 molecule) of fine

[1] This compound has since been described by Biltz in Ber. d. chem. Ges., **32**, 650; see also Nef: Ann. Chem. (Liebig), **308**, 291.

sodium wire. The mixture was then kept sealed and cold for three days. The sodium was gradually attacked, an intensely colored, violet-blue solid being formed. Upon pouring the entire mixture into very dilute sulphuric acid, the blue color disappeared immediately. The ethereal solution was extracted with sodium carbonate, and 1 gram of benzoic acid, melting-point 119°, was obtained by acidifying the sodium carbonate solution. When the ethereal solution was dehydrated and distilled, a mixture of phenylbenzoin and triphenylcarbinol remained. This was extracted with ligroin (boiling-point 60° to 80°) and a residue of triphenylcarbinol was left, which, when recrystallized from alcohol, gave 1.2 grams of this substance, melting at 158°. From the ligroin extracts 1.4 grams of phenylbenzoin, melting-point 83°, were obtained.

Brombenzene and sodium, then, react with benzil exactly as sodium phenyl does, giving relatively the same yields of phenylbenzoin, triphenylcarbinol, and benzoic acid.

Phenylbenzoin, $(C_6H_5)_2=\overset{\overset{OH}{|}}{C}-CO-C_6H_5$.

Phenylbenzoin is insoluble in water, but readily soluble in ether, alcohol, and hot ligroin. It crystallizes from the last solvent in radiating needles which melt at 87°. When the substance was dissolved in three parts of 25 per cent methyl alcoholic potash and warmed, a precipitate of potassium benzoate appeared in a short time. This was filtered off and converted into free benzoic acid, melting at 122°. The alcoholic filtrate gave, on addition of water, a white precipitate of benzhydrol, melting, when purified from ligroin, at 67°, and giving a blood-red color when warmed with concentrated sulphuric acid. The decomposition of phenylbenzoin by the action of the alkali may be represented as follows:

$$(C_6H_5)_2:C\begin{cases}OH\\COC_6H_5\end{cases} + HOK \rightarrow$$

$$(C_6H_5)_2CHOH + KOCOC_6H_5.$$

A blood-red color is observed when a solution of phenyl-

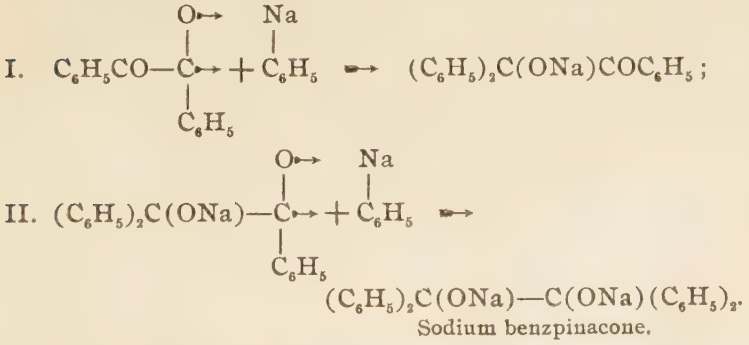
benzoin in concentrated sulphuric acid is warmed. This is also noticed in the case of benzilic acid, benzhydrol, etc., indicating dissociation into diphenylmethylene[1] and other products. The following experiment confirms this view: Phenylbenzoin (0.5 gram) was heated to 240° in a long tube, in a stream of oxygen, for three hours. When cooled, the residue was treated with ether, and there remained a small amount of tetraphenylethylene, melting at 210° to 215°. On extracting the ethereal solution with sodium carbonate and acidifying the alkaline solution, 0.2 gram of benzoic acid, melting-point 120°, was obtained. After distilling off the ether the residue was digested for three hours with phenylhydrazine and alcohol; 0.25 gram of benzophenonephenylhydrazone, melting at 135°, was obtained. The melting-point remained unchanged when it was mixed with a sample of the substance prepared from benzophenone and phenylhydrazine.

Analysis of the phenylbenzoin:

0.2040 gram substance gave 0.6224 gram CO_2 and 0.0992 gram H_2O.

	Calculated for $C_{20}H_{16}O_2$.	Found.
C	83.28	83.21
H	5.60	5.40

The action of sodium phenyl on benzil might result in the formation of two products, phenylbenzoin and benzpinacone, the course of the reaction depending upon whether 1 molecule of benzil reacts with 1 or 2 molecules of sodium phenyl.



Sodium benzpinacone.

[1] Nef: Ann. Chem. (Liebig), 298, 241.

The products actually obtained in the experiments described above are phenylbenzoin (I.), benzoic acid, and triphenylcarbinol, but no benzpinacone (II.). How are these facts to be explained? The sodium phenylbenzoin (I.) dissociates into diphenylmethylene and benzoate of sodium, as has been made probable by the above experiments with phenylbenzoin. The diphenylmethylene takes up oxygen from the air, giving benzophenone, which naturally must react at once with the sodium phenyl present to give triphenylcarbinol. Furthermore, benzpinacone dissociates spontaneously into benzophenone and benzhydrol, as has been shown above in the action of sodium and brombenzene on this compound. It is, therefore, exceedingly probable that benzpinacone sodium (II.) dissociates spontaneously into benzophenone and its disodium salt,

$$\begin{matrix}(C_6H_5)_2{=}C{-}O{-}Na \\ \quad\quad | \\ (C_6H_5)_2{=}CONa\end{matrix} = (C_6H_5)_2{=}C{=}O + \begin{matrix}(C_6H_5)_2C{-}O{-}Na \\ \quad\quad | \\ \quad\quad Na\end{matrix}.$$

Hence, even if reaction II. takes place under the existing conditions, it is impossible to expect a formation of benzpinacone.

The Action of Sodium Phenyl on Carbon Dioxide.

Sodium phenyl was made in the usual way from 10 grams of mercury phenyl and 10 grams of sodium in ligroin (boiling-point 70° to 80°) solution. On passing dry carbon dioxide into the mixture a reaction took place with considerable evolution of heat. The reaction-product was poured into water and extracted with sodium carbonate. The alkaline solution gave, when acidified, 6 grams of crude benzoic acid, which, by recrystallization, gave 4.5 grams of the pure acid, melting at 122°. When mixed with a sample of benzoic acid, the melting-point was not changed. The theoretical yield is 6.9 grams of benzoic acid. This experiment was tried three times, and in every case good yields were obtained. The action of carbon dioxide on sodium phenyl is analogous to that of carbon dioxide on sodium acetylenes,[1] sodium zinc alkyls,[2] and on phenyl aluminium chloride:[3]

[1] Lagermark: Ber. d. chem. Ges., **12**, 854; Nef: Ann. Chem. (Liebig), **308**, 281.
[2] Wanklyn: Ann. Chem. (Liebig), **107**, 125; **111**, 234.
[3] Friedel and Crafts: Ann. chim. phys., [6], **14**, 441.

$$O{=}C{=}O + Na{-}C_6H_5 = O : \underset{\displaystyle C_6H_5}{\overset{\displaystyle |}{C}}{-}ONa.$$

Kekulé[1] found that carbon dioxide acting upon brombenzene and sodium gave benzoic acid, diphenyl, and small amounts of benzophenone and phenyl benzoate. This shows that in a mixture of brombenzene, sodium, and carbon dioxide, the sodium first acts upon the brombenzene to give sodium phenyl. Part of the sodium phenyl reacts with unchanged brombenzene to give diphenyl, while another part reacts with the carbon dioxide to give benzoic acid.

Action of Sodium Phenyl on Chlorcarbonic Ether.

Wurtz[2] discovered that brombenzene, chlorcarbonic ether, and sodium amalgam give benzoic ether, and other homologues of brombenzene give corresponding homologues of benzoic ether.[3] The yields in all cases are very poor, as the chlorcarbonic ether gives a great deal of carbon monoxide and diethyl carbonate; mercury phenyl, etc., is also formed. It is now obvious that the sodium first reacts with the brombenzene, forming sodium phenyl, which then combines with the chlorcarbonic ether to give benzoic ether and sodium chloride.

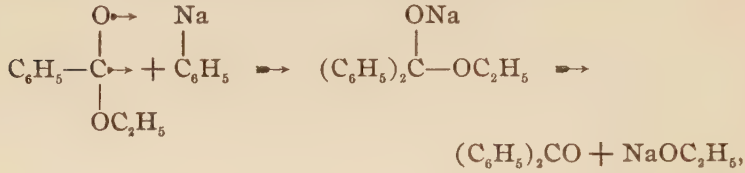
Five grams of mercury diphenyl in ligroin (boiling-point 60° to 80°) were converted into sodium phenyl. Three grams of chlorcarbonic ether in absolute ether were then slowly added, the solution becoming quite warm. When water was added and the solution extracted with sodium carbonate, no benzoic acid was obtained on acidifying the alkaline solution. The ligroin solution, when dried and distilled, gave only a small amount of benzoic ether, boiling at about 210°. It was identified by its odor and by conversion into benzoic acid (melting-point 118°) by means of methyl alcoholic potash. The residue from which the benzoic ether had been distilled was crystallized from alcohol, and 1.1 grams of triphenylcarbinol, melting at 158°, were obtained. The alcohol filtrate

[1] Kekulé: Ann. Chem. (Liebig) **137**, 178.

[2] Wurtz: *Ibid.*, Suppl., **7**, 125.

[3] Kekulé: Ber. d. chem. Ges., **7**, 1007; Jacobson: *Ibid.*, **17**, 2374; Nahnsen: *Ibid.* **17**, 2192.

was boiled with phenylhydrazine, but no benzophenonephenylhydrazone was obtained. Sodium phenyl and chlorcarbonic ether, as is obvious from the preceding, give very little benzoic ether. The benzoic ether first formed must, therefore, react further with sodium phenyl, as follows:



$$(C_6H_5)_2CO + NaOC_2H_5,$$

and the resulting benzophenone then reacts with more sodium phenyl, forming triphenylcarbinol. This is proved by the following experiment:

Action of Brombenzene and Sodium on Benzoic Ether.

When a solution of 3 grams benzoic ether and 6 grams brombenzene in absolute ether was allowed to stand sealed twenty-four hours with 2 grams of sodium wire, no metal was left. The solution was colored deep-blue and a blue precipitate covered the bottom of the vessel.

The reaction-products were found to be 1.4 grams triphenylcarbinol, melting at 158°, 0.2 gram of benzoic acid, 0.3 gram of triphenylmethane, melting-point 92° to 93°, and benzophenone, which was identified by means of its phenylhydrazone (0.42 gram melting at 135°). In a second experiment, where the same amounts of benzoic ether and brombenzene but more sodium, 3 grams instead of 2 grams, were used, no benzoic acid was obtained. The other products were triphenylcarbinol, 1.2 grams, triphenylmethane, 0.65 gram, and benzophenone, 1.4 grams, melting at 48° to 49°. The triphenylcarbinol was separated from the other two products by crystallization from alcohol. The alcoholic filtrate, in the second experiment, gave, on fractional distillation, 2.4 grams of material boiling between 280° to 350°—a mixture of benzophenone and triphenylmethane. This was partially separated by fractional distillation and further by fractional crystallization.

Action of α-Bromnaphthalene and Sodium on Benzophenone.

α-Naphthyldiphenylcarbinol.—When 10 grams of benzophenone, 12 grams of α-bromnaphthalene, and 5 grams of fine sodium wire in absolute ether stood one week in a sealed vessel, and the mixture was treated with water and extracted with potassium hydroxide, a small amount of benzoic acid was obtained. The ether was distilled off, and the residue, by distillation with steam, gave 1 gram of naphthalene, melting-point 80°. The part not volatile with steam was dissolved in ether and ligroin, and after long standing a substance crystallized out which melted at 135° when recrystallized from ether and ligroin. It was easily soluble in ether and alcohol, but insoluble in water and ligroin.

The same compound, α-naphthyldiphenylcarbinol, was formed when 5 grams of brombenzene, 5 grams of α-naphthylphenylketone, and 2 grams of sodium wire in absolute ether stood two days. When the ethereal solution was treated with water and extracted with sodium carbonate no acid was obtained. The ethereal solution was dehydrated and distilled. The residue, crystallized from ether and ligroin, gave α-naphthyldiphenylcarbinol, melting at 135°. When samples of the two products were mixed, the melting-point was not changed.

Analysis:

I. 0.1721 gram substance gave 0.5589 gram CO_2 and 0.0952 gram H_2O.

II. 0.1912 gram substance gave 0.6192 gram CO_2 and 0.1023 gram H_2O.

	Calculated for $C_{28}H_{18}O$.	Found. I.	Found. II.
C	89.00	88.57	88.32
H	5.86	6.14	5.95

Action of p-Bromtoluene and Sodium on Benzophenone.

Benzophenone (5 grams), *p*-bromtoluene (5 grams), and sodium (2 grams) in absolute ether stood two weeks in a sealed vessel. The solution became intensely blue and a blue precipitate was formed. When the solution was treated with

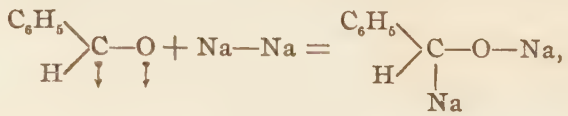
water and extracted with sodium carbonate no acid was found. When the ether was evaporated off and the residue dissolved in ligroin and ether, a substance at length crystallized out which melted at 74° when recrystallized from ligroin. This is *p*-tolyldiphenylmethane.[1]

The same substance was formed when 5 grams of *p*-tolylphenylketone, melting-point 58°, 3 grams of brombenzene, and 2 grams of fine sodium wire in absolute ether, were allowed to stand one week. The mixture was poured into water and extracted with sodium carbonate, but no organic acid was found. When the ether was evaporated off and the residue distilled with steam, about 1 gram of brombenzene was recovered. The residue was distilled in a vacuum and 1 gram of a liquid boiling at 195° to 200°, at 12 mm., was obtained, which, upon standing, gradually solidified. This was crystallized from ether and ligroin and gave 0.5 gram of *p*-tolyldiphenylmethane, melting at 74°. When samples of the two products were mixed, the melting-point was not changed. The yield is very poor in both cases and apparently no *p*-tolyldiphenylcarbinol is formed.

Five-tenths gram of the *p*-tolyldiphenylmethane was heated in a sealed tube with nitric acid (20 per cent) for twenty-four hours, at 150° to 160°. When the tube was opened a great deal of gas escaped. The product was then taken up in ether and extracted with sodium carbonate. When this alkaline solution was acidified, 0.2 gram of *p*-triphenylcarbinolcarbonic acid,[2] melting-point 200°, was obtained; this was further identified by its very insoluble barium salt.

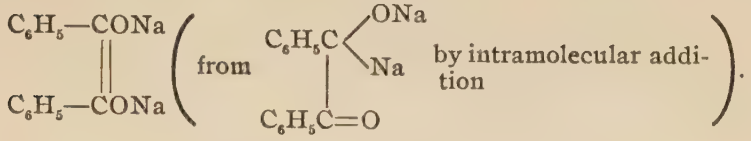
The Action of Sodium on Ketones.

The action of sodium on carbonyl compounds, as aldehydes, ketones, acid chlorides, and acid esters has been discussed by Nef. In Liebig's *Annalen der Chemie*, 308, 283 to 292, he presents the view that at first disodium addition-products, *e. g.*,

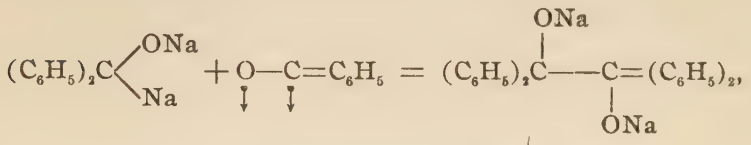


[1] Cf. E. and O. Fischer: Ann. Chem. (Liebig), 194, 263.
[2] Oppenheimer: Ber. d. chem. Ges., 19, 2029.

are formed which immediately react further with a second carbonyl group present in the same or in another molecule. Thus the benzil sodium of Beckmann and Paul was proved by him to be sodium dioxystilbene,

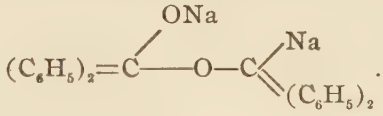


Similarly, benzophenone disodium must act with a second molecule of benzophenone,



Sodium benzpinacone.

to give sodium benzpinacone. Beckmann and Paul[1] ascribe the following very improbable constitution to the product obtained by them by the action of sodium on benzophenone,



Their salt gives, on treatment with water, benzpinacone and equal molecules of benzophenone and benzhydrol. The relative amounts obtained vary tremendously according to the amount of water used and possibly also according to other conditions. Furthermore, their dry salt gave, on treatment with dry carbon dioxide, equal molecules of benzophenone and benzilic acid. These results are self-evident on the basis of the ideas of Nef. We have but to conclude that sodium benzpinacone dissociates at ordinary temperatures into benzophenone and benzophenone disodium,

[1] Ann. Chem. (Liebig), **266**, 9 (1891).

$$(C_6H_5)_2{=}C(ONa){-}{-}C(ONa){=}(C_6H_5)_2 =$$

$$(C_6H_5)_2{=}C{=}O + Na{-}C(ONa){=}(C_6H_5)_2,$$

as is probable from the facts known regarding benzpinacone itself, as well as from the experiments described above with benzpinacone, sodium, and brombenzene. We must, in consequence, expect to obtain from this salt, by the action of water, varying quantities of benzpinacone and equal molecules of benzhydrol and benzophenone. With dry carbon dioxide (provided the non-dissociated salt does not act *per se*) we must obtain equal molecules of benzophenone and carboxylated benzilic acid, as follows:

$$2CO_2 + (C_6H_5)_2{=}C(ONa){-}{-}C(ONa){=}(C_6H_5)_2 =$$

$$(C_6H_5)_2{=}C{:}O + (C_6H_5)_2{=}C(O{-}Na)(Na) + 2O{-}C{=}O =$$

$$(C_6H_5)_2{=}CO + (C_6H_5)_2{=}C(O{-}C(=O){-}ONa)(CONa=O).$$

The carboxylated benzilic acid must lose carbon dioxide readily,

$$(C_6H_5)_2{=}C(O{-}COOH)(COOH) = (C_6H_5)_2{=}C(OH)(COOH) + CO_2.$$

The formation of equal molecules of benzophenone and of benzilic acid in this reaction as observed by Beckmann and Paul is, therefore, easily understood. Furthermore, in continuing experiments in this direction, we have been able to prove that a carboxylated benzilic acid (oily acid, readily los-

ing CO_2) is actually formed, thus establishing the correctness of the above conclusions.

Action of Sodium on Benzophenone.

Benzophenone (melting-point 48° to 49°, 5 grams) in absolute ether was treated with 2 grams of sodium (3 atoms) for three days. The solution became intensely blue and a blue solid was formed. The mixture was poured into water and extracted with sodium carbonate, but no organic acid was found. Upon evaporating the ether and crystallizing the residue from alcohol, 3 grams of pure benzpinacone (melting-point 185° to 186°) were obtained. By boiling the alcoholic filtrate with phenylhydrazine, only a small quantity of benzophenonephenylhydrazone was obtained. Upon distilling off the phenylhydrazine with steam and recrystallizing the residue from ether and ligroin, 1.6 grams of benzhydrol, melting at 66°, were obtained. Whether the large quantity of benzhydrol formed came from the action of water on benzophenone disodium,

$$(C_6H_5)_2{=}C(ONa){-}Na + H_2O \rightarrow (C_6H_5)_2{=}CHOH + 2NaOH,$$

or was formed by the reduction of the benzophenone by the nascent hydrogen liberated from the excess of sodium when the reaction-mixture was poured into water, is not certain.

Analysis of benzpinacone :

0.2252 gram substance gave 0.7001 gram CO_2 and 0.1225 gram H_2O.

	Calculated for $C_{26}H_{22}O_2$.	Found.
C	85.20	84.79
H	6.07	6.04

The Action of Sodium and Carbon Dioxide on Benzophenone.

A flask containing 5 grams of benzophenone and 7 grams (11 atoms) of fine sodium wire in 100 cc. absolute ether was attached to a return-condenser through which was passed a tube leading in well-dried carbon dioxide. The flask was well shaken, and the benzophenone sodium was evidently acted on

as fast as formed, for the blue color was never very intense. The mixture was poured into a separatory-funnel and water was added to dissolve the sodium salts. When the water solution was acidified, an oily acid, probably carboxylated benzilic acid, $(C_6H_5)_2=C<^{OCOOH}_{COOH}$, which did not change as long as the water was cold, was precipitated; but when the water was warmed the oil decomposed with a lively evolution of carbon dioxide, forming 3 grams of pure benzilic acid (theory 5.5 grams) that melted at 149° to 150°.

Analysis:

0.2345 gram substance gave 0.6330 gram CO_2 and 0.1132 gram H_2O.

	Calculated for $C_{14}H_{12}O_3$.	Found.
C	73.65	73.40
H	5.31	5.35

On the Isomeric Diacetyldioxystilbenes.

During the progress of Nef's work on sodium benzil and its conversion into diacetyldioxystilbene, two isomeric diacetyldioxystilbenes, melting at 110° and 153°, respectively, were independently discovered by Thiele.[1] We have repeated Thiele's experiments and proved that the lower melting isomer is identical with Nef's diacetyldioxystilbene, which, when perfectly pure (recrystallization from ether), melts at 118°.

The diacetyldioxystilbene of Nef has been examined crystallographically by Bowman in Groth's laboratory.[2] Two preparations, one made by Nef's and the other made by Thiele's method, were therefore submitted to Dr. O. C. Farrington, of the Field Columbian Museum, for comparison. His report (July 15, 1899) is as follows:

"The crystals of the two lots submitted by Mr. Acree proved to be entirely similar. They are all alike in habit, being made up of a short, stout prism, truncated to a somewhat tabular form by the prominent orthopinacoid. The orthodome $d(101)$ is also a prominent face, while $c(001)$ appears as a narrow face truncating the edge a d.

[1] Thiele: Ann. Chem. (Liebig), **306**, 142; cf. Nef: *Ibid.*, **308**, 290.

[2] Nef: Ztschr. für Krystallographie; cf. Ann. Chem. (Liebig), **308**, 290.

"As crystals of lot No. 1 had previously been measured by Bowman (*loc. cit.*) I confined my measurements to those of lot No. 2. Few faces on these crystals were suited to accurate measurement, oscillatory combinations usually causing a line of signals several degrees in length. The following measurements made on two different crystals may, however, be deemed characteristic. For comparison the values of similar angles calculated from Bowman's ratios are given :

	Measured.	Mean.	Calculated.
$a' : c = (100) : (001)$	86° 46′		
	86° 40′	86° 47′	86° 56′
	86° 55′		
$a : m = (100) : (110)$	70° 22′		
	70° 30′	70° 20′	70° 30′
	70° 8′		
$m' : m'' = (110) : (110)$	39°	39° 4′	39°
	39° 8′		
$m : n = (110) : (120)$	9° 20′		
	9° 40′	9° 30′	9° 28′
$a : d = (100) : (101)$	42° 25′	42° 25′	42° 25′

"The form K(102) noted by Bowman was not observed on the crystals. The calculated and measured values for the angles quoted above agree so closely that there can be no doubt that the crystals all have the same form."

Analysis of the diacetyldioxystilbenes, obtained by Thiele's method :

I. 0.2198 gram substance (melting-point 107° to 108°) gave 0.5837 gram CO_2 and 0.1139 gram H_2O.

II. 0.2191 gram substance (melting-point 118°) gave 0.5811 gram CO_2 and 0.1102 gram H_2O.

III. 0.2188 gram substance (melting-point 153°) gave 0.5848 gram CO_2 and 0.1032 gram H_2O.

	Calculated for $C_{18}H_{16}O_4$.	Found. I.	II.	III.
C	72.92	72.43	72.34	72.89
H	5.46	5.76	5.59	5.24

I wish to thank Dr. J. U. Nef for the great inspiration and encouragement he has given me during this work.